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Recent advances in optimal design of thermochemical conversion of biomass to chemicals and liquid fuels

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The main objective of this paper is to provide an overview of the methods for optimal design of thermochemical-based biorefineries. Generally speaking, heuristics/knowledge based, steady-state simulation based and mathematical programming are three main approaches. Following a general introduction of thermochemical biomass transformations and brief highlights of main achievements in optimal design of thermochemical-based biorefineries, the associated future opportunities and challenges are presented. An attempt is made with this paper to trigger further efforts to systematically synthesize and design thermochemical biorefineries to accelerate the commercialization of biorefinery technology and further reduce the reliance on petroleum-derived fuels.

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Introduction

Concerns about diminishing fossil fuel reserves along with climate change and national security have promoted considerable research activities on exploring alternative, environmentally friendly processes for producing liquid transportation fuels and value-added chemicals. Among these initiatives, conversions of sugar based and lipid based biorenewable resources have been given significant attention. Generally speaking, the developed technologies for biomass conversion can be categorized as thermochemical, biochemical, and catalytic routes [1–3]. The thermochemical route involves processing of the whole biorenewable resources at high temperature and/or pressure. The biochemical approach breaks down complex sugars, starch and cellulose to glucose which can be further converted into fuel molecules using enzymes and microorganisms. The catalytic route mainly contains reactions like aldol condensation, hydrolysis, dehydration, isomerization, reforming, hydrogenation, and oxidation [4].

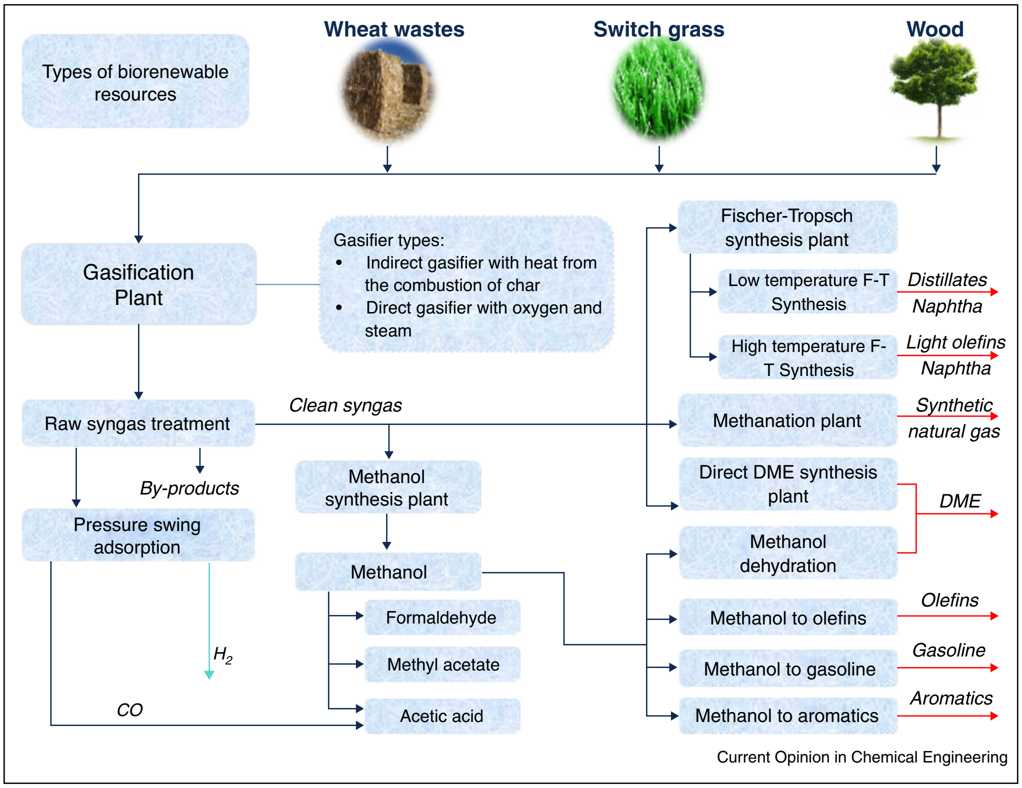
Although the thermochemical based routes also contain pyrolysis technologies, this paper only focuses on gasification driven biomass conversion processes. It should also be pointed out that this paper will not give a comprehensive review of biorefineries, but rather highlight the relevant achievements and future directions of optimal design/synthesis of biomass thermochemical conversion processes from a process systems engineering perspective. The structure of the paper is as follows: after a brief introduction of the thermochemical conversion processes, the methodologies for process synthesis are presented. In the next section, recent advances in the optimal design/synthesis of thermochemical conversion processes are discussed. Challenges and future research directions are then discussed briefly followed by the conclusion.

Thermochemical conversion routes

Thermochemical biomass conversion involves deconstructing feedstock and upgrading the resulting intermediates into a range of fuels and other products. As shown in Figure 1, the thermochemical conversion process contains three main processing parts, namely; firstly, gasification involving the devolatilization and conversion of biorenewable resources to produce raw syngas; secondly, syngas conditioning and treatment for removing solids and acid gases such as H_2S and CO_2; and finally, syngas upgrading toward olefins, aromatics, mixed alcohols and liquid transportation fuels.

Promoted by an oxidizing agent, endothermic gasification reactions take place at high temperature around 600–1000 °C. Oxidizing agents are traditionally air, nitrogen, carbon dioxide, oxygen, steam, or a combination of these compounds. With an oxidizing agent under high temperature, the reactions decompose the large polymeric molecules of biomass to produce raw syngas which is mainly composed of CO and H_2. CH_4, light hydrocarbons, ash, char, tar along with several contaminants. There are two general classes of gasifiers [5], that is, directly heated gasifiers and indirectly heated gasifiers. Directly heated gasifiers use the exothermic reactions between oxygen and organics to provide the necessary heat to devolatilize the biomass and to convert any residual carbon-rich chars. A disadvantage of directly heated gasifiers is the expensive oxygen production which typically requires a large plant size to improve economics. Unlike the directly heated gasifiers, the energy for an indirectly heated

Figure 1



Schematic representation of gasification based thermochemical conversion routes.

gasifier comes from the combustion of byproduct char and/or a portion of the product syngas with air. Since most indirectly heated gasifiers operate at low pressure, syngas compression units for downstream purification and fuel synthesis units are required.

Syngas cleanup and conditioning consists of multiple operations: tar reforming, syngas cooling/quench, and acid gas (CO_2 and H_2S) removal with subsequent sulfur recovery. The treated syngas can be used for electricity production, or for producing high-purity hydrogen/CO through purification units such as pressure swing adsorption. However, the main portion of the syngas will be used for chemicals and liquid fuels production via the corresponding processing pathways such as methanol synthesis, methanation plant, and Fischer–Tropsch synthesis.

Methanol is a very important platform chemical. The synthesis of methanol from syngas is highly exothermic. $Cu/ZnO/Al_2O_3$ is the most widely used catalyst for methanol synthesis. Although methanol can be used directly as a liquid fuel, it can also be converted into acetic acid, conventional transportation fuel range products through the methanol-to-gasoline (MTG) process [6], olefins through the methanol-to-olefins (MTO) process [7], 'on-demand' propylene through the methanol-to-propylene (MTP) process [8], and aromatics through the methanol-to-aromatics (MTA) process [9]. Among these technologies, several processes have been commercialized: Mobil MTG, UOP/Mobil MTO, Lurgi MTP, and Dalian methanol-to-olefins (DMTO). Besides, DMTO II, which additionally cracks C_4 to improve C_2/C_3 yields, developed by Dalian Institute of Chemical Physics is currently in its demonstration stage [10]. Tsinghua University in China has developed a fluidized bed based 'on-purpose' MTA process which will be commercialized very soon [11].

Fischer–Tropsch synthesis is a highly exothermic reaction to produce a wide variety of alkanes. For gasoline-range products, higher temperatures (300–350 °C) and iron catalysts are typically adopted. For diesel-range and wax products, lower temperatures (200–240 °C) and cobalt catalysts are typically used [12]. Operating pressures are typically in the range of 10–40 bar. The product distribution can be estimated using the Anderson–Schulz–Flory chain-growth-probability model, in which shorter hydrocarbon chains form as the temperature increases [13]. At high temperatures, selectivity favors methane and light gases. At low temperatures,